# ORGANIC CHEMISTRY - IV (MCH41)

## UNIT-I

## Aromatic character / Aromaticity:-

Benzene possess the following unique aromatic character. Planar, fully conjugated, monocyclic/polycyclic systems with $(4n+2)\pi$ electrons, having a closed shell of electrons, all in bonding orbitals are exceptionally stable. Such systems are said to be aromatic.

The characteristic properties are collectively called as aromaticity which are different from aliphatic and alicyclic compounds

### (1) Comparatively resistant to undergo addition reactions:-

Though benzene possess a high degree of unsaturation, it does not undergo addition reactions with HBr, halogens and decolourisation of $Br_2$ water. Catalytic hydrogenation occurs only at high tempt pressure.

### (2) Heat of combustion:-

Its heat of combustion is low as compared to that calculated for cyclohexatriene. The difference between observed value (3301.3 KJ/mole) and calculated value (3451.8 KJ/mole) is 150.5 KJ/mole is resonance energy.

### (3) High resonance energy:-

Its heat of hydrogenation (observed) is 208.3 KJ/mole is rather low compared with that calculated for 1,3,5 hexatriene (358.8 KJ/mole) The difference between calculated and observed value 150.5 KJ/mole is called as resonance energy. Due to this resonance energy, benzene is highly stable.

### (4) Structure:-

It is a flat, cyclic compound containing a conjugated system of double bonds with planar geometry that alone permits a full $\pi$ orbital overlap -

⑤ Electrophilic Substitution Reaction:-

It undergoes electrophilic substitution reactions mainly like nitration, sulphonation halogenation and friedel-Crafts reaction etc, and rarely nucleophilic substitution reactions but these reactions are not given by open-chain polyenes.

⑥ -OH substituted aromatic compounds (like phenols) are more acidic than alcohols whereas -NH2 substituted aromatic compounds like amine is are weaker bases than aliphatic amines.

(I) Benzenoid Aromatic Compounds:-

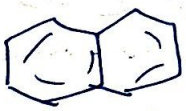
Benzene and all benzene like compounds which possess these features are benzenoid aromatic compounds. These compounds impart special stability unique to these compounds is refered to as aromatic character. (Aromaticity)

① Benzene:-

Benzene is a planar, conjugated, monocyclic compound with a π cloud of six electrons, obeys Huckels rule (4n+2) rule. (C is Huckel no). These 6π electrons are often refered to as aromatic sextet.

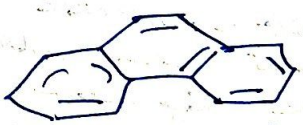
② Polycyclic Compounds:-

Polycyclic conjugated systems like naphthalene, anthracene and phenanthrene are the typical benzenoid aromatic compounds and the no & π electrons in each case are 10, 14 & 14



Naphthalene (10π e⁻)

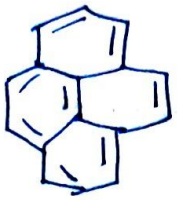
Anthracene (14π electrons)



phenanthrene (14π electrons)

③ Pyrene like structures:-

Pyrene with 16 π electrons does not obey Huckel rule and it may be expected not to show aromatic character. However it is a typical benzenoid aromatic compound as shown experimentally. In such polycyclic systems, the Huckel's rule is applied to only peripheral conjugated π electrons. Since it contains 14 peripheral π electrons, it is a benzenoid aromatic compound.

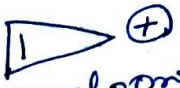


(II) Non-benzenoid aromatic compounds:-

These compounds obey Huckel's rule and show all aromatic characters but they do not have benzene like structure.

(i) cyclopropenyl cation:-

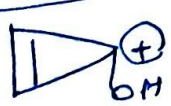
(a) This cation has a closed shell & $(4n+2)\pi$ electrons. Here $n=0$ and it contains $2\pi$ electrons.



cyclopropenyl cation

(b) Therefore it should be a stable aromatic system.

(c) several stable cyclopropenium salts have been prepared, which are non-benzenoid aromatic compounds.



1-Hydroxy cyclopropenyl bromide (stable)

cyclopropenyl hexachloroantimonate (stable)

(d) The NMR spectrum shows three equivalent protons.

(ii) Cyclopentadienyl anion is aromatic? Justify

(a) This anion has three doubly filled molecular orbitals so that it is cyclic

(b) It obeys Huckel's rule, $(4n+2)\pi$ electrons. ($n = 1$)

(c) This non-benzenoid aromatic compound is stable. Stable potassium cyclopentadienide and dicyclopentadienyl iron (Ferrocene) have been prepared.

cyclopentadienyl anion.

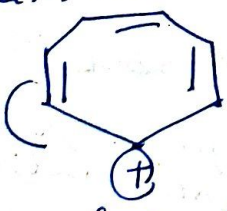
Potassium cyclopentadienide

Ferrocene

(d) It has 5 resonating structures as follows.

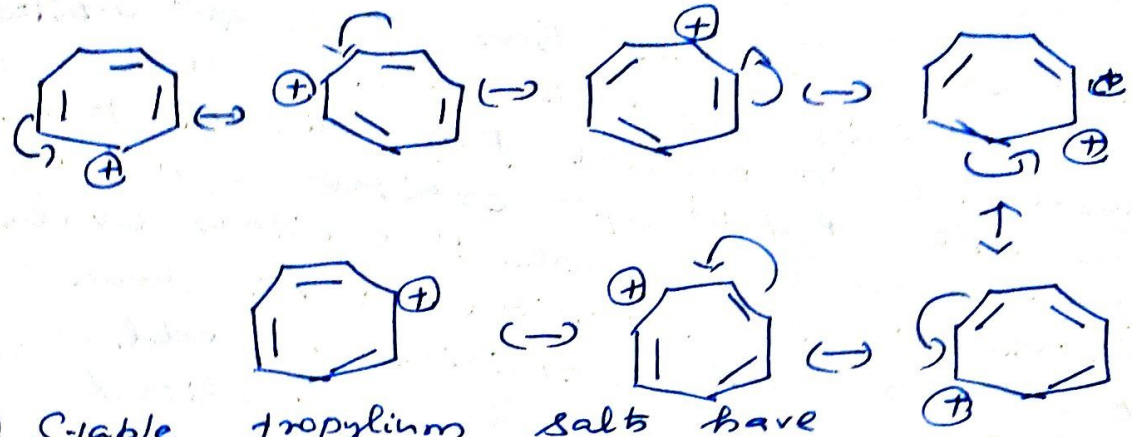
(e) Ferrocene shows aromatic substitution reactions like Friedel Crafts acylation.

(iii) cycloheptatrienyl cation:- (Tropylium ion) Explain the aromaticity of tropylium ion?

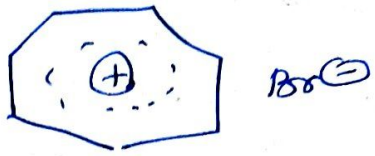


(a) This has 6 $\pi$ electrons and obeys Huckel's rule and is stable

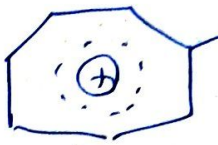
(b) It is flat and has seven resonating structures as follows.



(3) Stable tropylium salts have actually been prepared which show aromatic character.



Tropylium bromide (Stable)



Hydroxy tropylium chloride (Stable)

~~Huckel's theory of aro~~

## III Heterocyclic aromatic compounds:-

All heterocyclic compounds are aromatic since they obey Huckel's rule and have aromatic characters.

Examples:-

a) 

Pyrole

b) 

Furan

c) 

Thiophene

d) 

Pyridine.

e) 

Indole

f) 

Quinoline

g) 

Isoquinoline

(1) Explain the aromatic character of pyrole.?

(1) Pyrole has the following structure

(2) Pyrole is aromatic due to the presence of six delocalised $\pi$ electron clouds of $\pi$ electrons.

③ Nitrogen in pyrole has three $sp^2$ orbitals each containing an odd electron and an unhybridised 'p' orbital perpendicular to the plane of the hybrid $sp^2$ orbitals containing a pair of electron. These p orbitals overlap sideways with the p orbital of the four Carbon atoms each containing an odd electron to form a cyclic delocalised $\pi$ molecular orbital containing six electron

④ It shows aromaticity and it undergoes usual electrophilic substitution reactions like nitration, sulphonation etc.

⑤ It is even more aromatic than benzene because it undergoes coupling reaction with diagonium salts and nitrosation of the ring.

⑥ Unlike secondary amines, it lacks basicity since the lone pair of electrons are involved in delocalisation.

⑦ It is a flat molecule.

⑧ Its resonance energy is of the order of 79.8 KJ/mole according to heat of combustion data.

② Explain the aromatic character of furan & thiophene.

① Furan & thiophene have the following structures

Furan

Thiophene.

② Same as above. (Instead of $\underset{H}{N}$ we put O/S)

③

④ They undergo electrophilic substitution reaction.

⑤ Flat structure

⑥ Thiophene is more aromatic than furan due to more contributing resonating structures due to vacant 3d orbitals of sulphur.

(3) Explain the aromaticity of the following compounds.

(i) Azulene (ii) 

(i) Azulene:-

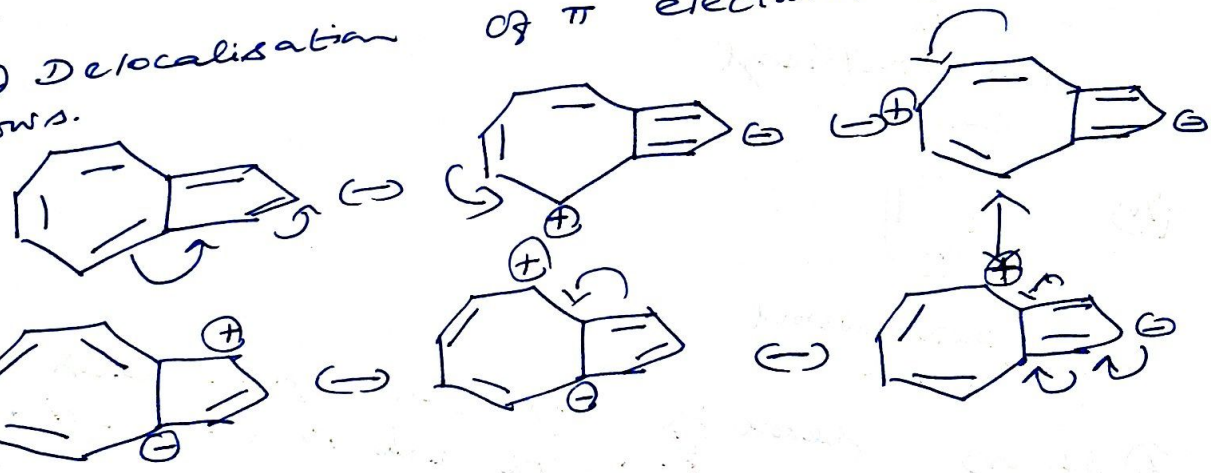
(a) Azulene is a bicyclic compound containing 10 π electrons ($n = 2$) which are effectively delocalised throughout the molecule. ∴ it is an aromatic compound.

(b) Azulene is considered as a combination of cycloheptatrienyl cation and cyclopentadienyl anion.

(c) The molecule exists as a dipolar structure with a dipole moment of 1.0 debye unit

(d) The seven membered ring has 7π electrons and the five membered ring has 5π electrons. Two π electrons are common to both the rings.

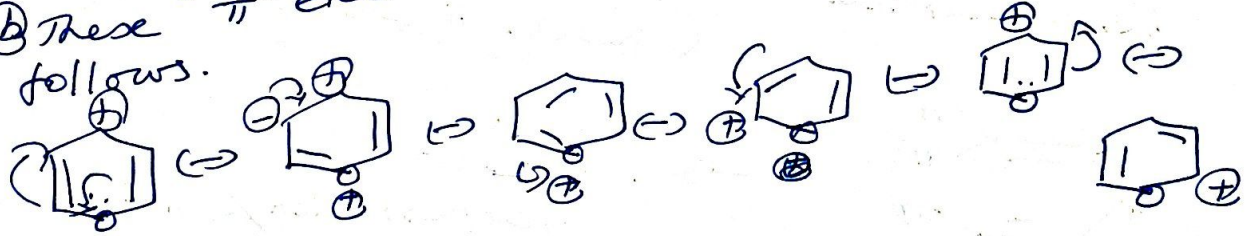
(e) Delocalisation of π electrons occurs as follows.



(ii) 

(a) It is aromatic since it contains 6π electrons $n = 1$ including the lone pairs of electrons on oxygen atom.

(b) These π electrons are delocalised as follows.

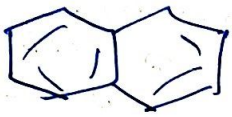
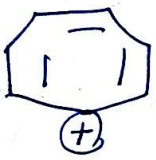


④ what are aromatic, antiaromatic and non-aromatic compounds.?

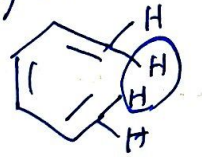
## Aromatic compounds:-

(a) The π clouds in a molecule or ion must contain a total of $(4n+2)$ π electrons, where $n = 0, 1, 2, 3 \cdots$, the molecule is said to be aromatic

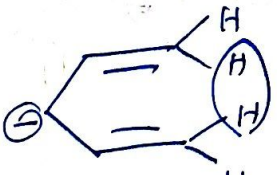
(b) Examples:-

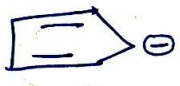
| Compound | No of π electrons |
|---|---|
| (i)  | 6 |
| (ii)  | 10 |
| (iii)  cycloheptatrienyl cation | 6 |
| (iv)  cyclopentadienyl anion | 6 |

(b) It on removing hydrogen from each end of the chain and joining the ends to form a ring, the ring formed has lesser π electron energy than the open chain, the ring is aromatic.


1,3,5-hexatriene


Benzene (6π electrons)
(Lesser π electron energy)

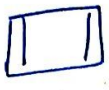

Pentadienyl anion
6π e⁻


cyclopentadienyl anion

## II ANTIAROMATIC SYSTEM:-

(i) If the π cloud in a molecule contains $(4n)\pi$ electrons, where $n = 0, 1, 2, 3 \ldots$ etc, the molecule is called as antiaromatic

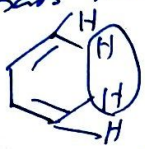
(Eg)



cyclotetradiene
4π e-

cyclooctatetraene
[8]-annulene
8π e-

(ii) If the ring has greater π electron energy than the open chain, the ring is anti-aromatic



1,3-butadiene
4π-electrons

→

cyclobutadiene
Greater π electron energy.

## III NON-AROMATIC:-

If the ring has same π electron energy as the open-chain, the ring is non-aromatic

(Eg) $H\overset{\oplus}{C}H-(CH=CH)_{15}-CH=CH_2$ → [30] Annulene

30π electrons

30 π electrons
Cπ electron energy same as in alicyclic system.

How do you account for the aromaticity of naphthalene?

(i) Naphthalene is polycyclic conjugated system having 10π electrons which obey Huckel's rule of aromaticity. $(4n+2)\pi$ electrons.

$n = 2$.

(ii) It is planar & cyclic cloud of delocalised π electrons.

(iii) It is a benzenoid aromatic compound and it contains 2 benzene rings.

(iv) It has resonance energy of 250 KJ/mole.

(v) It undergoes mainly electrophilic substitution

reactions like nitration, sulphonation, halogenation and Friedel - Crafts reaction etc.,

(vi) It has equal bond lengths.

(vii) It has $\pi$ electron energy less than its non-cyclic analogue.

Differentiate benzenoid, non-benzenoid, heterocyclic aromatic compounds, antiaromatic and non-aromatic compounds.

| S.No. | Benzenoid Aromatic Compound. | Non-benzenoid aromatic compound. | Hetero Aromatic |
|---|---|---|---|
| 01. | Contains cyclic and planar structure with conjugated system of $(4n+2)$ $\pi$ electrons delocalising effectively throughout the molecule and having benzene like structure. Examples:- Benzene, naphthalene etc., | (01) Compounds which do not have benzene like structure but possess conjugated system of $(4n+2)$ $\pi$ electrons, cyclic, planar, flat and $\pi$ electrons are delocalised within the ring. Examples:- cyclopropenyl cation, cyclopentadienyl anion. | (01) Compounds not have like and their carbon substitu hetero possess system $\pi$ electrons planar and $\pi$ delocalis ring. Examples Furan, |
| (02) | They sustain induced diamagnetic ring current | (02) They sustain induced diamagnetic ring current. | (02) They induced ring |
| (02) | They have equal bond lengths. | (03) They have equal bond lengths. | (03) They equal lengths |
| (04) | $\pi$ - electron energy is lesser than their open-chain analogue. | (04) $\pi$ - electron energy is lesser than their open-chain analogue. | (04) $\pi$- energy than open-chain |
| (05) | Nucleus independent Chemical shift values are negative. | (5) Nucleus independent Chemical shift values are negative | (5) Nucleus Chemical values |

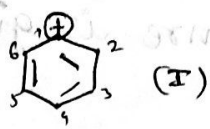
| S.No. | Benzenoid Aromatic Compound. | Non-benzenoid aromatic compound. | Hetero Aromatic Compound | Heterocyclic compound | Antiaromatic compound | Non-aromatic Compound |
|---|---|---|---|---|---|---|
| 01. | Contains cyclic and planar structure with conjugated system of $(4n+2)$ $\pi$ electrons delocalising effectively throughout the molecule and having benzene like structure. Examples:- Benzene, naphthalene etc., | ① Compounds which do not have benzene like structure but possess conjugated system of $(4n+2)$ $\pi$ electrons, cyclic, planar, flat and $\pi$ electrons are delocalised in the ring. Examples:- cyclopropenyl cation, cyclopentadienyl anion. | ① Compounds not have like and their Carbon Substitute Hetero Possess System $\pi$ electrons planar and $\pi$ delocalised ring. | which do benzene structure ring atoms are ted with atoms. conjugated of $(4n+2)$ , cyclic & flat electrons are ed in the | ① Compounds which possess conjugated system of $4n\pi$ electrons with effective delocalisation are called as antiaromatic. They are planar and cyclic Examples:- cyclooctatetraene, cyclobutadiene. | ① Compounds having cyclic or acyclic systems, conjugated / unconjugated double bonds and even sometimes no double bonds and may not have planar shape. Examples:- Methane, 30-[Annulene] |
| ② | They sustain induced diamagnetic ring current | ② They sustain induced diamagnetic ring current. | ② They induced ring | Examples:- Furan, pyrrole. sustain diamagnetic current- | ② They sustain induced paramagnetic ring current. | ③ They sustain no diamagnetic or paramagnetic ring current. |
| ③ | They have equal bond lengths. | ③ They have equal bond lengths. | ③ They equal lengths | have bond | ③ They have equal bond lengths. | ② They have unequal bond lengths. |
| ④ | $\pi$-electron energy is lesser than their open-chain analogue. | ④ $\pi$-electron energy is lesser than their open-chain analogue. | ④ $\pi$-energy than open-chain | electron is lesser their analogue | ④ $\pi$-electron energy is ~~lesser~~ greater than their open-chain analogue. | ④ $\pi$-electron energy is same as that of open-chain analogue. |
| ⑤ | Nucleus independent Chemical shift values are negative. | ⑤ Nucleus independent Chemical shift values are negative | ⑤ Nucleus Chemical values | independent shift are negative | ⑤ Nucleus independent Chemical shift values are positive | ⑤ Chemical shift values are zero. |

# UNIT - I

Dr. B.S

1) 1,3,5 - cyclohexatrienyl cation is aromatic but 1,3,5 - cyclo heptatrienyl carbon is not - Justify.

1,3,5 - cyclohexatrienyl cation structure is given below,



(I)

i) This molecule obeys Huckle's rule [(4n+2)π e⁻ rule], since it has 6π - e⁻s and Huckel no. n = 1.

ii) It is flat, planar, cyclic having conjugated double bonds and the π - electrons are delocalised. It has continuous π - e⁻ system.

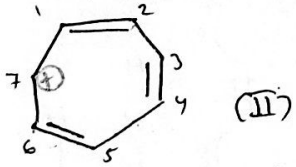
iii) Its energy is less than its open - chain analogue.

iv) Sustains diamagnetic ring current.

v) Chemical shift values are negative.

So, it is Aromatic.

1,3,5 - cycloheptatriene structure is given below,



(II)

Even though this molecule (II) obeys Huckel's rule and has 6 π electrons, the π electrons system is not continued.

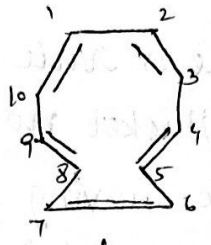
So, this molecule is not Aromatic.

2) Enumerate the aromaticity in Annulenes.

Annulenes are conjugated polyenes containing ten or more carbon atoms in the ring. They are named by writing the ring size followed by the word "annulene".

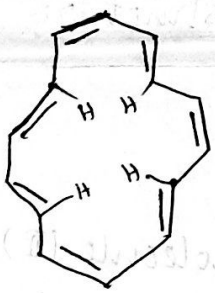
Examples : i) [10] - Annulene.

10-Annulene is not aromatic. Since the structure is not planar. Even if it contains 10 π electrons which is in accordance with Huckel's rule, it is not aromatic. Its structure is given below.

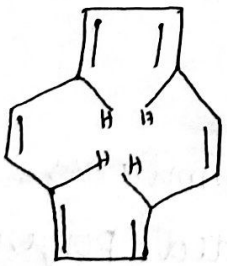



ii) [14]-Annulene :

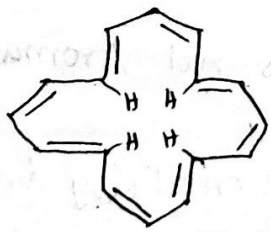
~~This~~ cpd has 14-annulene containes 14 π e⁻ and it obeys Huckel's rule. But it is not aromatic and highly unstable. Due to the steric hindrance of the four internal hydrogen atoms, the ~~polarity~~ planarity of the molecule is twisted and delocalisation is not possible and hence it is not aromatic.




iii) [12] & [16]-Annulene.



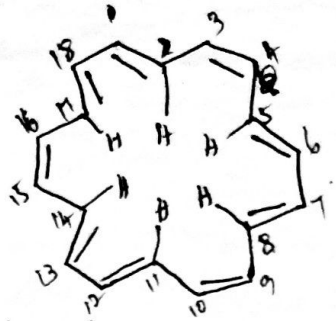

[12]-Annulene




[16]-Annulene.

Both the cpds have 4nπ electrons but ~~they are~~ it is not aromatic. They are not planar molecules due to non-bonding interactions of inner hydrogen.

iv) [18] - Annulene :



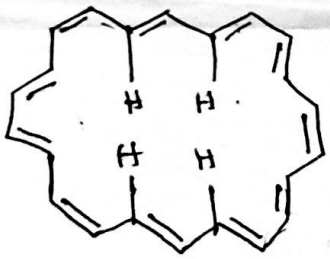
i) It obeys Huckel is rule since it has $(4n+2)\pi$ electrons and Huckel no, $n = 4$.

ii) It has cyclic & Planar structure.

iii) It has conjugated = bonds and $\pi$ electrons are delocalised.

iv) In NMR spectra, 12 outer protons are deshielded, downfield at $\delta$-value is higher. (8-9.0) and six inner protons are sheilded and up-field at 3.0 $\delta$ value.

v) [22] - Annulene ;



i) It obeys Huckel is rule and it has 22 $\pi$ $e^-$ and $n = 5$.

ii) It is planar, flat and cyclic.

iii) It has conjugated double bonds and $\pi$ electrons are delocalised.

iv) Hence it is aromatic.